Abstract

Nacre is a natural ceramic/organic composite made of constituents with poor mechanical properties yet is three orders of magnitude tougher than its main ingredient, aragonite. There have been many studies to identify the toughening mechanisms in nacre, and the organic interface is often cited as having the most significant effect on the overall toughness of nacre. In this study, we measure the inter-laminar toughness (ILT) of nacre from three different species using chevron notch technique. Using LEFM analysis, we also show that the measured intrinsic ILT accounts for only 3% of the overall interface toughness while the remaining originates from a synergy of extrinsic toughening mechanisms.

1 Introduction

Nacre possesses a lamellar structure resembling a brick-wall where 0.2-0.9 µm thick aragonite tablets are cemented together with thin 30 nm organic layers [1]. Mineral tablets in nacre are arranged in a staggered manner which provides the structure with a unique mechanism of deformation and outstanding combinations of stiffness, strength and toughness [1]. Recent puncture tests performed on red abalone shells revealed a large number of interfacial cracks propagating in the direction transverse from the penetration direction and extending along the interface of the tablets [2]. The interfaces in nacre therefore largely control its mechanical responses, whether it is deformed or cracked, along or across the layers.

2 Sample preparation and experimental setup

In this study, three types of mollusk shells were selected for fracture test: red abalone, pearl oyster and top shell. Using a precision diamond saw, 9×5×3 mm plates from the nacreous layer of the shells were cut and a 60° chevron notch was introduced in the specimens. The specimens were tested using a miniature loading stage at a fixed displacement rate of 3 µm. Another set of half-chevron specimens was also prepared by cutting chevron specimens across their width, by polishing their surface down to 0.05 µm for performing in-situ tests under an optical microscope.

3 Chevron notch fracture test

The load displacement curves of the specimens showed a linear response followed by a nonlinear region which was more pronounced in top shell. While crack propagation was relatively stable for top shell and pearl oyster, red abalone showed a catastrophic failure. Among the three shells, top shell showed the highest maximum load while red abalone failed at a load nearly one order of magnitude lower. The ILT of the three nacres was calculated from the maximum load $F_{\text{max}}$ and the elastic properties and geometry of the chevron notch specimen, using [3]:

$$J_{\text{IC}} = F_{\text{max}}^2 \left( \frac{1}{2w(a)} \frac{\partial C}{\partial a} \right)_{\text{min}} = F_{\text{max}}^2 I_{\text{min}}$$  \hspace{1cm} (1)

Where $C$ and $w$ denote the compliance of the specimen at crack length $a$. In order to determine $I_{\text{max}}$, a 3D model of the chevron specimens was constructed in the commercial finite element software ABAQUS. The specimens were modeled as a transversely isotropic material ($E_z=30\text{GPa}$, $E_p=70\text{GPa}$, $G_{pz}=10\text{GPa}$, $\nu_p=\nu_{zp}=0.2$). The obtained ITL is reported in Figure 1, and for comparison the crosslaminar toughness (CLT) of these shells is also included. The CLT is believed to be higher than the ILT mainly because of many toughening mechanisms which are active when the crack travels across the layers. However for top shell the ILT is higher than the initial CLT. This interesting observation was further investigated using in-situ half-chevron test.
4 In-situ half-chevron test and SEM imaging

Half-chevron tests were used to image inter-laminar crack extension in-situ. In red abalone, cracks followed growth lines which are weak organic layers. This explains why ILT in red abalone is significantly lower than those of pearl oyster and top shell, in which no growth line was observed. Interestingly, uncracked ligament bridging and crack deflection were observed for both pearl oyster and top shell. Additionally for top shell, a diffuse white “process zone” ahead of the crack tip was captured through in-situ differential interference contrast (DIC) imaging. This process zone dissipated energy and is likely to contribute to the superior toughness of top shell compared to the other two types of nacre. Using SEM imaging, we also explored the fracture surface of the top shell and pearl oyster specimens. SEM micrographs revealed a more pronounced crack deflection in top shell which likely gives rise to its larger energy dissipation and higher toughness (Figure 2).

5 Organic interface toughness

The ILT measured here includes all the toughening mechanism, and a direct measurement of the interface was not possible. We therefore used a LEFM analysis to estimate the intrinsic toughness of the organic interface. The size of the inelastic region ahead of the crack tip (width $h$) was expressed as function of the stress-intensity factor at the tip. This leads to the simple expression:

$$K_{IC} = \frac{2\sqrt{h}}{0.79} \sigma_s$$

Using $\sigma_s = 60\text{MPa}$ and $h = 10\mu\text{m}$ (measured from the SEM images) leads to $K_{IC} = 0.43\text{MPa}\sqrt{\text{m}}$ which can be converted to an energy form using $J_{IC} = (1-\nu^2)K_{IC}^2/E$ for plane strain condition: $J_{IC} = 5.5\text{J/m}^2$. This value which is only 3% of the interface overall toughness (205 J/m$^2$) includes the process zone toughness of the top shell and is an upper bound for intrinsic toughness of the interface.

6 Conclusions

In this work, we measured the ILT of three species of nacre using miniature chevron specimens. The results showed that top shell possesses superior ILT. Using in-situ fracture test and SEM imaging, we showed that the high ILT of top shell stems from remarkable extrinsic toughening mechanisms such as process zone, uncrack ligament bridging and crack deflection. LEFM analysis was also used to measure the intrinsic toughness of the organic interface. The results showed that this toughness only accounts for 3% of overall toughness of the interface. The fact that top shell owes its high ILT to extrinsic toughening sources highlights the significant role of the structural design in determining the mechanical performance of the material. This finding will serve helpful in developing novel biomimicry layered composites.

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References

